

THE BEHAVIOUR OF ALKALI METALS IN BIOMASS CONVERSION SYSTEMS

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INTRODUCTION

The development towards reduced environmental impact and improved energy efficiency has in recent years lead to development of new power technology and a renewed interest in the use of biomass in the power supply.

The advantage of substituting coal by biomass are that the emission of CO_2 , which contributes to the greenhouse effect, is reduced. A disadvantage of biomass is that the problems concerning alkali metals often become more severe. That is due to the difference of how the alkali metals are bound in coal and biomass.

During combustion and gasification alkali metals may contribute to slagging, deposition, corrosion and fluidized bed agglomeration. Whether or where in the system the problems appear is related to the transformations of the alkali metals and these depend on fuel and process conditions.

The alkali metal remains in the ash fractions during the process or is released as gaseous alkali metal. The gaseous alkali metal reacts with the ash fractions or condense due to saturation. The alkali metals in the ash fractions, bottom ash and fly ash, may transform during the process dependent on which components are favoured.

Studies on the alkali metal transformations are carried out in order to predict and thereby reduce the mentioned problems. Tools to study the fate of alkali metals are measuring of gas phase alkali metal, equilibrium calculations and chemical analyses of solid materials as e.g. deposits.

The problems of alkali metals are known from coal conversion. With respect to coal the problems are mainly related to sodium and with respect to biomass the problems are mainly related to potassium. Hald (1994) contains a literature survey on alkali metals in coal conversion systems and compare coal and straw concerning alkali metals. A system for measuring of gas phase alkali metals was designed and the sampling efficiency was tested. A comprehensive equilibrium study was performed and the results organized in tables as an easy access to equilibrium results. How ash components contribute to melt formation is discussed. The use of the developed tools is demonstrated for a fluidized bed combustor and a gasifier. Theoretical and experimental discussions are mainly related to straw and coal, but the results may be used in the study of other fuels. Some results from Hald (1994) are presented below, arranged in the sections alkali metals in the fuel, alkali metals at equilibrium, gas phase measuring, alkali metals in a fluidized bed combustor and alkali metals in a straw gasifier.

ALKALI METALS IN THE FUEL

Using straw as fuel the alkali metal related problems become more pronounced than with coal, even though the content of the alkali metals may be quite similar. That is due to the difference of how the alkali metals are present in the fuels which is important for their fate during the conversion process.

The alkali metal alumina silicates are the alkali metal components in fuels which are the most stable and those with the highest melting points. Because of that alumina silicates are used as getter materials to reduce the amount of gas phase alkali metals and increase the melting points.

Alkali metals in a less stable form, easier released to gas phase during a conversion process, are those present as the more simple salts, e.g. KCl , NaCl and salts of carboxylic acids. Alkali metal not present as alumina silicates are in the following denoted the soluble alkali metals. Alkali metals as chlorides, carbonates and sulphates have relatively low melting points compared to the alkali metal alumina silicates.

Alkali metal related problems using coal are primarily due to sodium, although the potassium content often is higher than that of sodium. That is due to larger amounts of sodium in a soluble form.

In contrast to coal the content of Al_2O_3 in biomass is relatively small and the most alkali metals are present in a soluble form. Another important difference between coal and biomass is that getter materials may be present within the coal and react with the soluble alkali metal to form alkali metal alumina silicates.

The amount of melt formation depends on the combination of components and temperature. Equilibrium calculations will show which components are favoured.

ALKALI METALS AT EQUILIBRIUM

Equilibrium calculations may be used in the description of which components are favoured and what influence a change in process conditions will have. Exact amounts may be determined by gas phase measurements and chemical analyses of the solid materials.

An extensive equilibrium study was performed and some general tendencies for the alkali metals were revealed. The calculations involving more equilibrium equations were performed by use of an equilibrium model (Michelsen, 1989) assuming gas phase ideality and phases immiscible.

The ideal gas phase assumption was studied and shown to be acceptable for gasification/combustion gases, the relative deviation of the volume is maximum 4 % at pressures up to 80 atm in the temperature range 300 K to 2000 K. It was shown that with ideal liquid mixtures, containing alkali metals, present the gas phase content of alkali metals will be lower than if phases were immiscible.

General tendencies about which non-silicate alkali metal components to be favoured in ash materials or at condensation, at high and low temperature and at oxidizing or reducing conditions, could be arranged relatively to the ratios alkali metals to chloride (M/Cl) and alkali metals to sulphur (M_2/S), see Table 1. S, Cl and M describe the molar content of sulphur, chlorine and soluble alkali metals in the selected equilibrium system. The system can e.g. be the global system or a sub system as e.g. the gas phase. M_2 denotes M divided by two as alkali metals and sulphur form components in the mole ratios 2 : 1.

A general difference between coal and straw can be described by the mole ratios M_2/S and M/Cl , see Table 2. The sulphur content is lowest in straw and the chloride content in straw is in about the same range as in high chlorine coals.

Alkali metals, chlorine and sulphur from coal will be in the gas phase in the same ratios as given for the pure coal in Table 2. By use of Table 1 it is seen that alkali metals condensed from gas phase at coal combustion may be present only as M_2SO_4 . This agrees with what is described in the literature about sodium condensation in coal combustion systems.

With all soluble alkali metal, all sulphur and all chlorine from straw present in the gas phase, the mole ratios for the gas phase are as in Table 2. At combustion conditions Table 1 shows possibility for both alkali metal sulphates, carbonates and chlorides to condense when cooling the gas.

Results from measuring of potassium, chloride and sulphur in gas phase at straw combustion (those measurements mentioned in Jensen et al. (1995)) show that the chloride content typically exceeds the potassium content ($\text{M}/\text{Cl} < 1$). This leaves no possibility for alkali metal carbonate formation when the gaseous potassium condenses (see Table 2, $\text{M}/\text{Cl} < 1$ and $\text{M}_2/\text{S} > 1$). This is an example of how the equilibrium calculations and gas phase measurements may be used in the evaluation of deposition mechanisms.

Alkali metals are in the gas phase as $\text{MCl}(\text{g})$ and $\text{MOH}(\text{g})$. The distribution depends on the M/Cl ratio and the temperature. At temperatures above 800 °C no MCl will be found in solid or liquid form (see Table 1). This is true for a combustion or a gasification system using fuels with alkali metal contents similar or lower than straws. Both release of alkali metal from the fuel and the condensation of gaseous alkali metal are determined by kinetics. The equilibrium information about alkali metal chloride tells that with sufficient residence time of the fuel ash all alkali metal chlorides will be released to gas phase at temperatures above 800 °C and cooling a gas the alkali metal chlorides will not condense at temperatures above 800 °C.

Other examples of how the equilibrium calculations may be used to describe a change in the conversion system are 1) that more alkali metals will be present in gas phase with an increasing chloride to alkali metal ratio. 2) With coal as fuel, changing from reducing to oxidizing conditions, the amount of alkali metals present in gas phase may decrease due to condensation of alkali metal sulphates. With straw as fuel this change will not be as significant as straw contains much less sulphur than coal.

The tendency to melt formation will increase with increasing amounts of the alkali metal components with low melting points present. Those alkali metal components act as fluxing agents for the other ash components. Calculating freezing point depression by equation (1) it may be evaluated to which extent the ash component denoted i contributes to melt formation.

$$\Delta T = T^* - T = - \frac{R}{\Delta H_m} \cdot T^* \cdot T \ln(x_i) \quad (1)$$

ΔT is the freezing point depression, T^* the melting point of the pure solid i (equals freezing point), R the gas constant, ΔH_m the molar melting enthalpy for component i and x_i the mole fraction of the component i in the mixture. At temperatures above T no solid phase of component i will be present. The freezing point curve for a component i can be described by the set of T, x_i . Freezing points of a number of components at $x_i = 0.8$ were calculated, the results are given in Table 3. A material as Al_2O_3 has a high melting point and a high melting enthalpy leading to a very small freezing point depression. A component as SiO_2 has a low melting enthalpy which give a large freezing point depression.

One important differences between coal and straw is that SiO_2 in straw is present as pure SiO_2 instead of as alumina silicates. The melting point of SiO_2 is significantly reduced by the presence of components with low melting points and may therefore contribute to melt formation also at the lower temperatures.

GAS PHASE MEASURING

A sampling system for gas phase measuring was designed in order to measure the amount of alkali metals in the gas phase. The sampling system comprises a probe and bubblers. The probe carries an alumina condenser, which is moderately inert to alkali metals.

A verification of gaseous alkali metal sampling systems has been needed as alkali metals may condense as small aerosol particles possibly evading the sampling system. Therefore a laboratory system to study the sampling efficiency was developed. The sampling efficiency was studied with $KCl(g)$ in the range of 250 - 500 ppm(v) and with $NaCl(g)$ in the range of 0.5 - 250 ppm(v). The results show that 94 ± 6 % of alkali metals are captured with a gas flow of 5 Nl/min.

Soluble alkali metal in particles sampled coincident with the gas phase alkali metal may contribute to the measured gas phase result and in every sampling it may be evaluated to which extent.

Sampling with filter should be investigated, this could be done with the laboratory system used for studying sampling efficiency. Different things may be taken into account, typical filter materials react with or adsorb the gaseous alkali metal and a filter cake may react with or release gaseous alkali metal until equilibrium is obtained. In the alkali metal measurings mentioned in Jensen et al. (1995) the use of a quartz filter was tested, the results will be reported later.

ALKALI METALS IN A FLUIDIZED BED COMBUSTOR

The alkali metal behaviour is described for a 80 MW Circulating Fluidized Bed Combustor (CFBC), Grenaa Denmark. The CFBC is fed with a fuel mixture of coal and straw (heating value of about 50 % of straw and coal, respectively). Limestone is added for in bed removal of sulphur. The use of coal in combination with straw decreases the tendencies of bed material agglomeration, deposition and corrosion.

Potassium and chloride contents were measured in the CFBC, after the cyclone in front of two heat exchangers. The content of potassium was in average 100 ppm(v) and of chloride in average 110 ppm(v). This is about 25 % of total soluble potassium introduced and about 60 % of the total chloride introduced.

The gas temperature at the measuring point was about 800 °C, the maximum gas temperature in the system, about 920 °C, was in the top of the cyclone. Nordin (1993) reports for a fluidized bed system that the temperature at the surface of a burning particle may be about 150 °C higher than the gas temperature. This means that the particle temperature could have been above 1000 °C.

Deposits on the two heat exchangers were analyzed and the results are given as oxides. The first heat exchanger met by the gas contained about 5 % potassium as K_2O and the second about 30 %. The analyses of the deposits and equilibrium calculations indicated condensed alkali metal sulphates not to form to the extent of equilibrium at the location of measuring. The rate of condensation is such that the potassium is found in the deposit on the second heat exchanger.

A scanning electron microscopy analysis of the first micron layer (tube side) of the deposit on the second heat exchanger showed a first layer of potassium sulphate.

The introduced fuel combination has the ratios $M_2/S < 1$ and $M/Cl > 1$. When adding limestone for the capture of sulphur it can be explained as the ratio M_2/S increases, but gas phase measurements indicated a M_2/S ratio < 1 . By use of Table 1 it is seen that gaseous potassium will deposit only as potassium sulphate. This agrees with the chemical analyses of the deposit.

The kind of bed material may influence on the extent of melt formation, bed materials were evaluated and the influence of addition of limestone discussed. The bed material should have a relatively high melting point together with a relatively high melting enthalpy (see equation (1)) as e.g. CaO and Al_2O_3 (see Table 3). It may be considered which components may be formed as e.g. CaO will react with sulphur to form $CaSO_4$. A material which captures the alkali metals forming compounds with higher melting points may be preferred. Addition of limestone gives a possibility for reduction of the extent of melt formation as 1) the ratio $CaSO_4$ to K_2SO_4 increases (eutecticum at 875 °C), 2) the concentration of ash in the bed material decreases and 3) CaO itself contributes only to melt formation to a minor extent (see Table 3).

ALKALI METALS IN A STRAW GASIFIER

Potassium measurements were performed in a 50 kW moving bed straw gasifier, Laboratory of Energetics, The Technical University of Denmark. The gasifier was operating 12 hours during which the ash materials were accumulated in the system. The maximum temperature was about 950 °C in the top of the reactor where the fuel was introduced. The temperature was reduced downwards in the reactor, and the produced gas left in the bottom where the gas temperature was about 750 °C.

The potassium content was measured to 450 ppm(v) in the outlet gas at a temperature of 750 °C, that is 35 % of the total potassium content in the straw. The result is in reasonable agreement with equilibrium calculations at a temperature of 750 °C. It can not be known whether the measured potassium content has been released on the way downwards in the reactor or if it is an equilibrium established due to the accumulation of ash material.

Equilibrium calculations for the total system show that potassium in condensed form will be present as chlorides and carbonates if potassium silicates are not included in the calculations. This could also be found by the use of Table 1 and Table 2. If potassium silicates are included in the calculations the carbonates will not form. This is one of the general results, the alkali metal silicates are favoured to the carbonates.

The amount of potassium in the gas phase at 750 °C is the same whether potassium silicates are included in the calculations or not. The possible potassium silicates are $K_2O \cdot (SiO)_x$, where $x=2$ below 950 °C and $x=4$ above 950 °C.

CONCLUSION

Results of equilibrium calculations combined with gas phase measurements of the alkali metals, chlorine and sulphur were demonstrated as useful tools in the investigation of the alkali metal behaviour at gasification and combustion.

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Table 1 Mole ratios M_2/S and M/Cl describing which condensed non-silicate alkali metal components are favoured at low or high temperatures (T) and at reducing (Red.) or oxidizing (Ox.) conditions.

		$M_2/S \leq 1$ $M/Cl \leq 1$	$M_2/S \leq 1$ $M/Cl > 1$	$M_2/S > 1$ $M/Cl \leq 1$	$M_2/S > 1$ $M/Cl > 1$
Ox.	$T < 800^\circ C$	M_2SO_4	M_2SO_4	M_2SO_4 MCl	M_2SO_4 M_2CO_3 MCl
Ox.	$T > 800^\circ C$	M_2SO_4	M_2SO_4	M_2SO_4	M_2SO_4 M_2CO_3
Red.	$T < 800^\circ C$	MCl	M_2CO_3 MCl	MCl	M_2CO_3 MCl
Red.	$T > 800^\circ C$	-	M_2CO_3	-	M_2CO_3

Table 2 Mole ratios M_2/S and M/Cl in coal and straw.

	Coal	Straw
M_2/S	< 1	normally > 1
M/Cl	< 1	> 1

Table 3 Freezing points at $x_i = 0.8$ and ΔT at $x_i = 0.8$. Melting enthalpies and melting points for the pure components (T^*).

Component	ΔH_m (kJ/mol)	T^* ($^\circ C$)	$T_{x_i=0.8}$ ($^\circ C$)	$\Delta T_{x_i=0.8}$ ($^\circ C$)
$K_2O \cdot (SiQ)_4$	49.0	770	730	40
KCl	26.3	771	699	72
$CaCl_2$	28.5	772	705	67
NaCl	28.2	801	730	71
Na_2CO_3	29.6	850	776	74
$Na_2O \cdot (SiQ)_2$	35.6	874	809	61
Na_2SO_4	23.8	884	788	96
K_2CO_3	27.6	901	815	86
$NaBO_2$	33.5	967	887	80
$K_2O \cdot (SiQ)_2$	41.0	1045	971	74
K_2SO_4	34.4	1069	978	91
$MgSO_4$	14.6	1127	916	211
$CaSO_4$	27.6	1457	1277	180
SiO_2	9.6	1723	1167	556
Al_2O_3	111.1	2054	1967	87
CaO	79.5	2614	2432	182
MgO	77.8	2852	2635	217

ΔH_m -values are from Barin (1989) and T^* from Weast (1983).